Hydrazine-based Synergistic Ti(III)/N Doping of Surfactant-Templated TiO₂ Thin Films for Enhanced Visible Light Photocatalysis

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Abstract

This study reports the preparation of titanium (Ti^{3+}) and nitrogen co-doped cubic ordered mesoporous TiO_2 thin films using N_2H_4 treatment. The resulting co-doped TiO_2 (Ti^{3+} -N- TiO_2) thin films show significant enhancements in visible light absorption and photocatalytic activity. Cubic ordered mesoporous TiO_2 thin films were prepared via a sol-gel method with Pluronic F127 as the pore template. After brief calcination, the TiO_2 films were dipped into hydrazine hydrate which acts both as a nitrogen source and as a reducing agent, followed by heating at low temperature (90 °C). The hydrazine treatment period was varied from 5 – 20 hours to obtain different degrees of reduction and nitrogen doping. X-ray photoelectron spectroscopy (XPS) analyses and UV-vis absorbance spectra of Ti^{3+} -N- TiO_2 films indicate that the incorporated N atoms and Ti^{3+} reduce the band gap of TiO_2 and thus enhance the absorption of visible light. The corresponding visible light photocatalytic activity of Ti^{3+} -N- TiO_2 films was determined from the photocatalytic degradation of methylene blue under visible light illumination (at 455 nm). The Ti^{3+} -N- TiO_2 films prepared with 10 hours of treatment show the optimum photocatalytic activity, with a pseudo-first order rate coefficient of 0.12 h^{-1} , which is 3 times greater than that of undoped TiO_2 films. Calcination temperature and time were varied prior to hydrazine treatment to confirm that a brief calcination at low temperature (10 min at 350 °C) gave the best photochemical activity. In photoelectrochemical water oxidation using a 455 nm LED, the Ti^{3+} -N- TiO_2 films prepared with 10 hours of N_2H_4 treatment show about 4 times the photocurrent compared to undoped TiO_2 films. The present study suggests that hydrazine induced doping is a promising approach to enable synergistic incorporation of N and Ti^{3+} into the lattice of surfactant-templated TiO_2 films and enhanced visible light photoactivity, but that the benefits are limited by gradual mesostructure deterioration.

Keywords: chemical synthesis; thin films; nanostructures; electrochemical properties; non-crystalline materials

1. Introduction

Directly harvesting solar energy remains a promising approach to meet the increasing demand for clean and sustainable fuels and energy [1-3]. Since Fujishima and Honda first demonstrated its use for hydrogen generation from photocatalytic water splitting, TiO_2 has attracted much attention for solar energy harvesting due to its high photostability, low cost, and high availability [4-7]. These unique properties have enabled TiO_2 to be utilized in a wide range of applications including solar energy conversion, antimicrobial surfaces, whiteners in paint, ceramics, glass, textiles, sunscreen, medicine, and organic pollutant degradation for environmental remediation [2, 8-19]. The primary challenge of using TiO_2 for solar energy conversion is its high band gap [8]. The ultraviolet light that titania can absorb represents only 5% of the solar spectrum, whereas visible light constitutes about 47% [20]. A known strategy to overcome this limitation is to dope titania with nonmetal and metal dopants to introduce new electron energy levels, reduce the band gap, and allow the material to absorb visible light [7, 8, 21, 22]. Common nonmetal dopants include C, F, N, S, P and B [8]. Among the nonmetal dopants, nitrogen is the most effective dopant due to its comparable atomic size to oxygen, low ionization potential, and high stability [7, 9, 17, 23-35]. The mechanism of nitrogen doping is thought to be band gap reduction via the formation of a new energy state above the valence band of titania by mixing the $2p$ orbital of the nonmetal dopant with the O $2p$ orbital [8, 36].

Along with nitrogen, titanium (Ti^{3+}) introduced into the TiO_2 lattice can create an energy state below the conduction band of titania which further reduces the band gap [1, 5, 16, 37-43]. This Ti^{3+} state in TiO_2 improves not only light absorption but also charge transport. For instance, Zuo

et al. prepared a self-doped (Ti^{3+}) TiO_2 photocatalyst and demonstrated its use for hydrogen production under visible light [37]. More recently, Ti^{3+} doped TiO_2 prepared by hydrazine reduction has been reported [1]. When TiO_2 is reduced by any reducing agent, Ti^{3+} is expected to be formed along with oxygen vacancies. However with hydrazine (N_2H_4), titania is expected to be co-doped with both Ti^{3+} and N and is therefore to synergistically absorb more visible light and potentially be a more effective redox catalyst than TiO_2 doped with either species alone. Aman et al. explored this concept using Ti^{3+} and nitrogen doped TiO_2 nanoparticles for enhanced photocatalytic activity under visible light [6].

In addition to enhancing the optical absorption of TiO_2 , it is very important to control the morphology and the nanostructure of TiO_2 photocatalysts, which significantly impacts photocatalytic performance. Ordered nanostructured TiO_2 thin films prepared by surfactant templating are considered to be very effective structures for photocatalytic applications [9]. First, surfactant templating offers excellent control over the structure and morphology of the films such as tunable pore size, pore orientation, interfacial structure and pore connectivity. The pore structure facilitates the fast diffusion of reactants to the photocatalytic reaction sites of TiO_2 films. Second, the mesoporous structure of the TiO_2 films offers a high reactive surface area available for photocatalysis. Third, the sidewalls of mesoporous TiO_2 films are thin and comparable to the diffusion length of photogenerated holes and electrons, thereby suppressing charge recombination processes [44, 45]. Here, cubic ordered mesoporous TiO_2 thin films are prepared using evaporation induced self-assembly with TiCl_4 and triblock copolymer surfactant Pluronic F127 as a template. Although mesoporous titania films have been reported for photoelectrolysis, those films had discontinuous, disordered pores and high wall thickness [46, 47]. In contrast, the pores of our mesoporous titania thin films are continuous, ordered with cubic symmetry and surrounded by thin

walls. The thin walls in these films are expected to provide better charge transport and separation for photocatalysis. At the same time, the continuous, ordered pore space is expected to facilitate rapid diffusion of reactants to the surface and products away so that the entire thickness of the film can be utilized for reaction.

In the present study, we report the incorporation of Ti^{3+} and nitrogen atoms into surfactant-templated mesoporous TiO_2 thin films by hydrazine treatment. All prior studies of Ti^{3+} and N co-doping by hydrazine treatment used TiO_2 powders, nonporous films, nanowires or anodized nanotube arrays [1, 5, 6, 28, 39, 40, 48-54]. We hypothesize that surfactant templated mesoporous TiO_2 films have several advantages over TiO_2 nanotubes. First, mesoporous titania films have smaller pores and thinner pore walls (both 10 nm or less) than titania nanotubes which should result in higher surface areas and lower charge recombination rates [45]. Moreover, surfactant templated mesoporous titania films can be prepared on any substrate whereas anodized nanotubes can only be prepared on Ti foil or substrates amenable to thin film vapor deposition. The incorporation of Ti^{3+} and nitrogen using a single source, hydrazine, along with the development of the well-defined high surface area found in surfactant-templated ordered mesoporous TiO_2 thin films, are expected to result in a material exhibiting greatly enhanced visible-light absorption and photocatalytic activity. Because the films are formed *de novo* from a molecular precursor, they are expected to be more susceptible to doping, reduction, and structural modification than more fully crystalline materials available in other forms. To test this hypothesis, cubic ordered mesoporous TiO_2 thin films were synthesized by templating films derived from TiCl_4 with triblock copolymer surfactant Pluronic F127. Then, the films were treated with hydrazine hydrate, followed by analysis of photocatalytic activity for methylene blue degradation as a test reaction. Further, the optical absorbance and photocatalytic activity of Ti^{3+} -N- TiO_2 films were correlated with the

duration of hydrazine treatment. To understand the importance of the thermal treatment prior to hydrazine modification, the effects of calcination temperature and time of the titania films on the photocatalytic activity of hydrazine-treated titania films were studied. Finally, the photoelectrochemical performance of the doped films was demonstrated using water oxidation under basic pH conditions with a visible light source.

2. Experimental

2.1. Materials

Anhydrous ethanol (99.99%, 200 proof, Absolute, Anhydrous, ACS/USP Grade, Pharmco Aaper), F127 (triblock copolymer with average structure $\text{HO}-(\text{CH}_2\text{CH}_2\text{O})_{100}(\text{CH}_2\text{CHCH}_3\text{O})_{65}(\text{CH}_2\text{CH}_2\text{O})_{100}\text{H}$, $M_n = 12,500$ Da, Sigma-Aldrich), titanium tetrachloride (tech grade, 99.9%, Sigma-Aldrich), deionized ultrafiltered (DIUF) water (Fisher Scientific), colloidal graphite (Ted Pella, inc.), $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 80% (Hydrazine, 51%) (Fisher Scientific), methylene blue hydrate (Sigma Aldrich), Nochromix powder (Fisher Scientific), and concentrated sulfuric acid (Certified ACS Plus, Fisher Scientific) were all used as received.

2.2. Synthesis of mesoporous titania films

Nochromix solution, prepared according to the directions of the supplier, was used for the cleaning of borosilicate glass slides (Fisher Scientific). Sol preparation was begun by preparing a solution of 0.67 g of surfactant F127 in ethanol (18.43g). TiCl_4 (1.12 ml) was added to the previously prepared F127 solution in a nitrogen-filled glove bag. The solution was stirred for 10 min to allow for chloride / ethoxy exchange to take place. 1.8 g of deionized water was then added to the solution slowly. The solution was stirred again for 10 minutes. In-situ HCl is formed from the reaction between TiCl_4 and H_2O . This HCl makes the solution acidic which helps to control

the condensation reaction and allow the formation of continuous films. The cleaned glass slides were dip coated using a home built system at a rate of 6 cm/min from this solution to prepare the TiO₂ films, followed by aging in a highly humid environment (RH ~ 94%) in a refrigerator at a temperature of 4 °C for 2 h. The high RH environment was provided by placing the slides in a sealed box with two beakers containing water. Aging at high humidity and low temperature helps to promote ordered mesostructure formation, transformation and orientation by slowing the condensation of the precursor and controlling evaporation of the solvent. Immediately after aging, TiO₂ films were calcined in a muffle furnace (Vulcan 3-550) for 10 minutes at 350 °C. The temperature of the furnace was increased to 350 °C at a ramp of 25 °C/min but the calcined TiO₂ films were cooled rapidly after 10 minutes at the final temperature. Rapid transfer directly from the refrigerator to the furnace was carried out to avoid moisture condensation on the surface of the films [55].

For titanium reduction and nitrogen doping, a film was dipped into a hydrazine hydrate solution (N₂H₄·H₂O (80%)) deep enough to cover the titania film for 1 hour at room temperature. Then, the film was removed from the solution and heated at 90 °C for different periods (5, 10, 15 and 20 hours) in a closed 50 mL polypropylene centrifuge tube with a 1 ml reservoir of N₂H₄·H₂O (80%) in its conical shaped bottom. The excess liquid hydrazine was present to prevent rapid evaporation of N₂H₄ from the films but did not come into direct contact with the slides during heating. After treatment the film was heated at 90 °C for 10 minutes after being taken out of the centrifuge tube to remove the adsorbed water and hydrazine. The untreated TiO₂ sample and the TiO₂ samples treated for 5, 10, 15, and 20 hours are denoted as undoped TiO₂, and x h_Ti³⁺-N-TiO₂, where x is the duration of hydrazine treatment.

2.3. Characterization

For the imaging of nanoporous structure, scanning electron microscope (SEM) characterization was performed using a Hitachi S-900 at 6 kV. SEM samples were prepared by cutting the glass slide to the desired shape using a glass cutter and then mounting the sample exactly at the center of a SEM stub coated with carbon tape. The samples were aged at 120 °C overnight (~12 h). A Helios Nanolab 660 (FEI) was used for cross sectional sample preparation and STEM imaging. TEM was performed using an ultra-high resolution JEOL 2200FS. Low angle XRD analysis was performed using a Bruker-AXS D8 DISCOVER diffractometer to determine the degree of mesostructural ordering. Films were scanned at 0.25 °/min in 2 θ increments of 0.02° from 1° to 4°. The optical absorbance of the samples was obtained with an UV-vis absorption spectrometer (Ocean Optics, DT-MINI-2-GS). The measurement was carried out by placing the films at an angle of ~45° relative to the incident beam. X-ray photoelectron spectroscopic (XPS) analysis was conducted using a ThermoScientific K-Alpha photoelectron spectrometer using monochromatic Al K- α radiation with photon energy of 1486.6 eV. Before performing the experiment, the samples were cleaned with ethanol to remove dust from their surface.

2.4. Photocatalytic testing

The photocatalytic activity of the Ti³⁺-N-TiO₂ film was evaluated by monitoring the photo-degradation of methylene blue (MB). A photograph of the experimental set-up is shown in Supplementary Information Fig. S1. A blue LED (BLED) with wavelength of 455 nm and an ultraviolet LED (UVLED) with wavelength of 365 nm (Thorlabs) were used as the light sources. Power densities of the UVLED and BLED were measured with a power energy meter (standard photodiode power sensor, Si, Thorlabs) to be 6 mW/cm² and 22.5 mW/cm², respectively. The spectra of the UVLED and BLED reproduced from Thorlabs are given in Supplementary Information Fig. S2. A cylindrical beaker was used as the reactor. The top of the beaker was

covered with parafilm to avoid the evaporation of water. In each experiment, the solution volume and the initial concentration of MB were 25 ml and 1×10^{-5} M, respectively. The area of mesoporous TiO_2 films illuminated by the light source was $\sim 15 \text{ cm}^2$. The distance between the light source and the reactor was 1 cm. Before illumination, the solution was stirred for 30 minutes in the dark so that MB could be adsorbed onto the pore surface. The solution was continuously stirred using a magnetic stirrer throughout the experiment. The change in MB concentration was determined by periodically taking a 2 mL sample and measuring the optical absorbance at 664 nm using a spectrophotometer (Ocean Optics DT-MINI-2-GS). The sample was returned to the reactor after each measurement.

2.5. Photoelectrochemical testing

For photoelectrochemical (PEC) testing, TiO_2 and $\text{Ti}^{3+}\text{-N-TiO}_2$ films were prepared on fluorine-doped tin oxide (FTO) slides. Prior to dip coating, the FTO slides were cleaned with deionized water, acetone and isopropanol followed by UV-ozone treatment for 20 minutes to remove any organic contaminants. The water oxidation reaction was performed to evaluate the $\text{Ti}^{3+}\text{-N-TiO}_2$ film for photoelectrochemical performance in a photoelectrochemical system with a three electrode potentiostat (model CHI660D, CH Instruments, Inc.). TiO_2 films, platinum and Ag/AgCl were used as working, counter and reference electrodes, respectively. A glass cell was used as a reactor. KOH of 1 M concentration was used as the electrolyte. All three electrodes were kept in the reactor. The light source was a blue LED (ThorLabs) with 455 nm wavelength and 22.5 mW/cm^2 intensity. Current-time measurements were carried out using undoped TiO_2 and $\text{Ti}^{3+}\text{-N-TiO}_2$ films with an applied potential of 0.4 V vs. the Ag/AgCl reference electrode. The light was turned on and off every 300 seconds periodically to obtain the light and dark currents. This experiment was performed for 1800 seconds.

Electrochemical impedance spectroscopy measurements were carried out using the same potentiostat and electrolyte solution used for photoelectrochemical measurement. The measurement was performed at 1 Hz frequency in the dark. The potential was varied between -1.5 V and -0.3 V (vs Ag/AgCl).

3. Results and discussion

The structure and surface morphology of the TiO₂ films were characterized by SEM as shown in Fig. 1(a). Nanopores are clearly visible on the top surface of the film. The average pore diameter and wall thickness of the TiO₂ films are around 7 nm and 5.5 nm, respectively. The TEM image in Fig. 1(b) also clearly shows the presence of pores throughout the film. The arrangement of the pores is consistent with a cubic array of interconnected globular mesopores [45]. The cross-sectional bright field STEM image (Supplementary Information Fig. S3) also shows that the cubic array of pores extends across the thickness of ~ 80 nm thick films. Fig. 1(c) shows the XRD pattern of the TiO₂ film, which corroborates that the mesoporous titania films have an ordered pore structure. A single XRD reflection was observed at $2\theta = 2.26^\circ$ which corresponds to a d-spacing value of 3.9 nm. Assuming that the mesostructure is oriented so that the SEM image gives the (110) d-spacing, this peak corresponds to the (420) plane parallel to the substrate for a body-centered cubic mesophase (*Im3m* space group), but this may be a different peak because of contraction normal to the film. Since the pore size found from SEM images is almost three times of the d-spacing, the reflection in Fig. 1(c) is definitely a higher order XRD diffraction peak, indicating that a well-ordered structure is present. Wide angle XRD ($2\theta > 10^\circ$) was performed to investigate the phase of the mesoporous TiO₂ film but the films were found to be x-ray amorphous.

Fig. 1. Electron micrographs of the F127-templated TiO_2 film after calcination and without hydrazine treatment: (a) SEM image of the top surface, (b) TEM image of material scraped from the glass substrate, and (c) XRD pattern of TiO_2 film on the original substrate.

To identify the crystalline phase in the titania films, high-resolution TEM (HRTEM) and selected area electron diffraction (SAED) were performed. In a representative HRTEM image (Fig. 2), a large amount of amorphous phase is observed. However, the film also contains dispersed nanocrystals with a size of about 2 nm. Supplementary Information Fig. S4 shows an enlarged HRTEM image of a nanocrystal in the film. The lattice fringe is 0.245 nm, which is consistent with anatase (103) or (004) d-spacing.[56] In addition to the direct visualization by HRTEM, the SAED pattern from the same sample (Fig. S5) was collected but showed only a diffuse ring rather than any bright diffraction spot, probably due to the small amount of nanocrystals embedded in an amorphous matrix.

Fig. 2. HRTEM image of undoped titania film.

Fig. 3 presents the optical absorbance and the estimated band gap of hydrazine treated TiO₂ films. The UV-vis spectra indicate that the primary absorption feature associated with the band gap of the material shifts towards the visible wavelength range upon hydrazine treatment. In addition, modification of the films causes enhancement of absorbance in the range from 350-700 nm, along with enhancement of ultraviolet absorption. This enhancement in the absorbance is due to the reduction and nitrogen doping of the film. Enlarged spectra of the Ti³⁺-N-TiO₂ films in the visible light region are shown in the inset of Fig. 3 (a). The inset reveals that the absorbance tail is extended towards longer wavelengths as the duration of hydrazine treatment increases. The absorbance of the 10 h_Ti³⁺-N-TiO₂, 15 h_Ti³⁺-N-TiO₂ and 20 h_Ti³⁺-N-TiO₂ films are almost the same up to 550 nm. However, the 15 h_Ti³⁺-N-TiO₂ and 20 h_Ti³⁺-N-TiO₂ films showed a new band in the range of 550-700 nm. This suggests that the films treated for more than 10 hours may exhibit an enhanced photo-response at long wavelengths.

In order to determine the band gap of the undoped TiO₂ and Ti³⁺-N-TiO₂ films, Tauc plots were drawn (Supplementary Information Fig. S6). To do this, $(\alpha h\nu)^{1/2}$ vs. $h\nu$ was plotted where α is the absorption coefficient and $h\nu$ is the photon energy. The absorption coefficients were calculated from the absorbance divided by the film thickness from Supplementary Information Fig. S3. The band gap was estimated by extrapolating the linear portion of the Tauc plot to the x-axis where the value of $(\alpha h\nu)^{1/2}$ approaches zero [57]. The relation between band gap and hydrazine treatment duration is shown in Fig. 3(b) and clearly shows an effect of hydrazine treatment on the band gap of Ti³⁺-N-TiO₂. The band gap of undoped TiO₂ film is 3.5 eV, which is consistent with an amorphous / nanocrystalline structure (wide angle XRD revealed no discernable reflections from crystalline phases). All of the doped films showed a band gap between 3.30 and 3.40 eV. Though the band gap of all the doped films are almost same, localized midgap states might be

formed in the doped films treated for longer time, and specific surface sites could be generated representing catalytically active arrangements of Ti, N and O. This might be the reason for higher absorbance across the visible region of the $\text{Ti}^{3+}\text{-N-TiO}_2$ films treated for increasing times.

Fig. 3. (a) UV-vis spectra of undoped TiO_2 and $\text{Ti}^{3+}\text{-N-TiO}_2$ films prepared using different hydrazine treatment times (the inset shows an enlarged region in the visible wavelength range) and (b) band gap vs. hydrazine treatment time based on Tauc plot analysis.

XPS was used to determine the nitrogen content and chemical state of undoped TiO_2 and 5 h $\text{Ti}^{3+}\text{-N-TiO}_2$ films. As shown in Fig. 4(a), XPS surface scanning shows a peak with high intensity at ca. 400 eV for 5 h $\text{Ti}^{3+}\text{-N-TiO}_2$ films whereas no peak was found for undoped TiO_2

films. The composition of nitrogen in 5 h-Ti³⁺-N-TiO₂ films was measured using the XPS peaks of Ti, O and N to be 2.32 atomic %. Several authors reported that the binding energy of nitrogen in TiO₂ are in the range of 396 - 404 eV [9, 57, 58]. There are two types of nitrogen found in doped titania - (i) substitutional doping with a binding energy of 396 eV, and (ii) interstitial doping with binding energy of about 400 eV [8]. The XPS peak at 400 eV is due to N-N, N-O, or Ti-O-N bonding whereas direct Ti-N bonding gives rise to a binding energy of 396 eV [40]. Compared to other hydrazine based studies, our hydrazine treated Ti³⁺-N-TiO₂ films showed significantly higher nitrogen content. For instance, Sun et al. reported about 0.2% nitrogen species in N-TiO₂ synthesized using hydrazine as the nitrogen source [39]. That might be because our amorphous/nanocrystalline surfactant templated TiO₂ films were formed *de novo* from a molecular precursor, which is expected to enhance nitrogen incorporation and hydrazine reduction compared to more fully crystalline materials available in other forms. Depth profiling was performed inside the films using argon ion etching for 10 etching intervals of 5 seconds each at 1000 eV energy. Fig. 4(b) shows that N 1s peaks are found at both 400 eV and 396 eV, which implies that both interstitial and substitutional nitrogen are present in the 5 h-Ti³⁺-N-TiO₂ film. Nitrogen is found throughout the film, but a higher amount of nitrogen is found at the film surface, as shown in Fig. 4(c). This might be due to the combined nitrogen from doping and adsorbed species the atmosphere. The fraction of substitutional nitrogen increases with increasing etching depth within the film, suggesting that N₂H₄ creates interstitial N/O species near the surface but still is able to introduce nitrogen into the matrix of the films throughout their depth. The etching depth of TiO₂ film has been estimated by comparing with the standard etching rate of Ta₂O₃. According to the XPS instrument documentation, the etching rate for Ta₂O₃ is 1.05 nm/s for the same potential

(1000 eV) used for TiO₂ film etching. Since the TiO₂ film is also a metal oxide as Ta₂O₃, it is assumed that the etching rate of TiO₂ will be similar, suggesting a total etched depth of 47 nm.

Fig. 4. (a) High resolution N 1s XPS spectra, (b) XPS N 1s depth profile spectra for 5 h_Ti³⁺-N-TiO₂ film, and (c) plot of nitrogen content from XPS depth profile vs. total Ar etching time at 1000 eV power.

Figs. 5(a) and 5(b) show the XPS spectra in the Ti 2p range during 1000 eV Ar etching depth profiling of undoped TiO₂ and 5 h_Ti³⁺-N-TiO₂ films, respectively. The spectra have two obvious peaks at ca. 458.8 eV and 464.5 eV associated with the Ti 2p_{3/2} and Ti 2p_{1/2} orbitals, respectively in both undoped TiO₂ and 5 h_Ti³⁺-N-TiO₂ films [6]. A shoulder at about 457 eV was found to the right of the peak at 458.8 eV for both undoped TiO₂ and 5 h_Ti³⁺-N-TiO₂ films. This shoulder is associated with the Ti³⁺ state [6]. It is possible that Ti³⁺ is observed in both films because of partial reduction due to Ar etching. However, the relative peak intensity and width of the Ti³⁺ shoulder of 5 h_Ti³⁺-N-TiO₂ are visibly higher than those of undoped TiO₂ film. This indicates that 5 h_Ti³⁺-N-TiO₂ films have more reduced Ti³⁺ compared to undoped TiO₂ films. A direct comparison of the XPS spectra of undoped and doped TiO₂ films has been made to more clearly compare the Ti³⁺ peaks within the film. Supplementary Information Fig. S7(a) shows the XPS Ti 2p depth profile spectra of the undoped TiO₂ and 5 h_Ti³⁺-N-TiO₂ films after 45 s of etching. Though the absolute intensity of the shoulder for Ti³⁺ in the 5 h_Ti³⁺-N-TiO₂ film is a little higher than that for the undoped TiO₂ film, the relative intensity of Ti³⁺ in the 5 h_Ti³⁺-N-TiO₂ film is much higher compared to the peak intensity of Ti³⁺ in the undoped TiO₂ film. Peak fitting was performed to deconvolute the contributions of Ti 2p_{1/2}, Ti 2p_{2/3} and Ti³⁺ in the Ti 2p spectrum. Supplementary Information Fig. S7(b) and (c) show the peak fitting of the XPS Ti 2p spectra (after 45 s of etching). The relative contribution of Ti³⁺ in the undoped TiO₂ and 5 h_Ti³⁺-N-TiO₂ film are 11.3% and 23.2%, respectively. While Ar ion etching may introduce some reduced titanium, this indicates

that the doped film has significantly more Ti^{3+} compared to an undoped titania films after 45 s of etching.

Aman et al. also observed a shoulder at 457 eV for Ti^{3+} state in addition to the original peak at 459.7 eV in hydrazine treated TiO_2 . They suggested that the Ti^{3+} formation is mostly due to the hydrazine reduction [6]. Mao et al. prepared reduced titania by hydrazine treatment but could not detect Ti^{3+} in the hydrazine reduced TiO_2 using XPS analysis [1]. They used electron paramagnetic resonance (EPR) to show the presence of Ti^{3+} . Several studies also used EPR to determine the presence of Ti^{3+} in hydrazine treated TiO_2 [1, 39, 49, 51]. However, due to the limited quantity of material present in these films, EPR analysis was not possible.

Fig. 5. XPS Ti 2p depth profile spectra of (a) undoped TiO_2 films and (b) 5 h- Ti^{3+} -N- TiO_2 films.

The characterization above established that hydrazine treatment leads to increases in nitrogen content, Ti^{3+} doping and visible light absorption. The visible light driven photocatalytic activity of Ti^{3+} -N- TiO_2 films was assessed by monitoring photocatalytic degradation of methylene blue (MB) and compared with that of undoped TiO_2 films. Prior to each photocatalytic measurement, the TiO_2 films were immersed in MB-containing solution for at least 30 min, in order to make sure that the adsorption of MB onto the surface of mesoporous TiO_2 films became saturated. MB adsorption reached equilibrium in 30 min, as shown in the representative long-time adsorption study in Supplementary Information Fig. S8(a). For photocatalytic measurements, the MB-containing solution was exposed to a blue LED light (peak wavelength 455 nm) to measure photocatalytic activity over the course of 4 hours. Fig. 6(a) shows the photocatalytic results normalized using the absorbance at the time that illumination with the LED began, and with the time scale set to zero at the beginning of illumination. The curves clearly show enhanced photocatalytic activity of Ti^{3+} -N- TiO_2 films compared to the undoped TiO_2 film. Insignificant degradation was found without TiO_2 films (direct photolysis of MB). The photocatalytic degradation results of MB with undoped TiO_2 film and Ti^{3+} -N- TiO_2 films clearly showed that the photocatalytic activity of Ti^{3+} -N- TiO_2 gradually increased in proportion to the duration of hydrazine treatment from 0 to 10 hours.

The kinetics of photocatalytic degradation reaction rates were quantified by fitting the decay of MB concentration with the pseudo-first order rate equation: $C=C_0*\exp(-kt)$, where k = the rate coefficient. Supplementary Information Fig. S8(b) shows that all experiments display very good linear fits between $\ln(C/C_0)$ and t , thus indicating that first order kinetics are appropriate in this case. The rate coefficients are plotted as a function of hydrazine treatment time in Fig. 6(b). The

rate coefficients increase with increasing hydrazine treatment until 10 hours. This correlates with the increase in visible light absorbance, and decrease in band gap found above. The 10 h- Ti^{3+} -N- TiO_2 films showed the maximum rate coefficient of 0.12 h^{-1} , which was nearly 3 times greater than for undoped TiO_2 film. Based on the film thickness (80 nm), structure (from SEM) and illuminated area, this corresponds roughly to a rate coefficient of $\sim 85 \text{ min}^{-1}/(\text{g catalyst})$. The increase in photocatalytic activity after hydrazine treatment could be attributed to the enhancement of the visible light absorbance due to a combination of nitrogen doping and titanium reduction to Ti^{3+} , facilitated by the nanocrystalline mesoporous architecture. The enhancement observed here is comparable to the results reported in a previous studies. For instance, Selvam et al. prepared N-doped TiO_2 by a wet method using hydrazine. The N- TiO_2 showed 70 % nitrobenzene conversion (5 h photoirradiation) whereas untreated TiO_2 showed 60 % conversion (6 h photoirradiation) under 365 nm mercury lamp irradiation, which represents a $1.6\times$ increase in activity (assuming 1st order kinetics) [52]. Xu et al. observed about $4\times$ enhancement in X-3B dye solution degradation under visible light irradiation (MVL 210 source) for TiO_2 nanotubes after the samples were hydrazine treated [5]. In another study, Sun et al. prepared Ti^{3+} and N co-doped titania particles by hydrazine treatment. In the 4-chlorophenol degradation under 250 W Xe lamp irradiation, the first order rate constant for doped titania was 0.002 min^{-1} whereas undoped titania did not show any significant photodegradation [39]. It is difficult to compare our results directly with the literature due to the use of different light sources with different intensity and catalyst amount, but the effects of hydrazine treatment appear to be comparable or better than in prior reports.

Fig. 6. Methylene blue degradation kinetics with undoped TiO_2 (0 h) films, Ti^{3+} -N- TiO_2 films, and solution without catalysis (Photolysis): (a) Concentration profile, and (b) pseudo-first order rate coefficient vs. hydrazine treatment time.

While hydrazine treatment helps titania in visible light driven photocatalytic activity, excessive exposure to hydrazine negatively affected its photocatalytic performance. For instance, 20 h- Ti^{3+} -N- TiO_2 films showed a rate coefficient of 0.054 h^{-1} , which was much lower than that for the 10 h- Ti^{3+} -N- TiO_2 films. The photocatalytic performance of the 10 h- Ti^{3+} -N- TiO_2 , 15 h- Ti^{3+} -N- TiO_2 , and 20 h- Ti^{3+} -N- TiO_2 films are not proportional with the UV-vis spectroscopy measurement as they exhibited about the same absorbance at 455 nm wavelength (Fig. 3(a)). Since the reaction rate

strongly depends on the available surface area of the film and the network connectivity, deterioration of the porous network might explain the decline in activity with long exposure to hydrazine (and water vapor). The mesostructure of the $\text{Ti}^{3+}\text{-N-TiO}_2$ films was investigated by SEM as shown in Fig. 7. More high resolution SEM images are provided in Supplementary Information Fig. S9. The pore wall thickness increased and pore size decreased due to the coarsening during the long time hydrazine treatment. These effects cause pore constriction and partial pore blocking. The coarsening increases with the hydrazine treatment period. After 20 hours of the treatment, the film almost lost accessibility of the pores completely at the scale visible by SEM. This structural deterioration caused a decrease in available surface area, which would explain the decrease in photocatalytic activity. Thus, the photocatalytic performance of the $\text{Ti}^{3+}\text{-N-TiO}_2$ films displays a tradeoff between increasing absorbance due to doping and reduction, and decreasing surface area due to coarsening of the mesostructure. The reduction of surface area most likely dominates over the increase in visible light absorbance in the 15 h_ $\text{Ti}^{3+}\text{-N-TiO}_2$ and 20 h_ $\text{Ti}^{3+}\text{-N-TiO}_2$ films which causes the decrease in photocatalytic activity in the MB degradation reaction.

Fig. 7. Plan view SEM images of (a) undoped TiO₂, (b) 5 h_Ti³⁺-N-TiO₂, (c) 10 h_Ti³⁺-N-TiO₂, and (d) 20 h_Ti³⁺-N-TiO₂ films (Scale bar: 120 nm).

The effect of calcination temperature of the titania films on the photocatalytic activities of the 10 h_Ti³⁺-N-TiO₂ films was studied by methylene blue degradation using BLED illumination. First, three titania films were prepared using 10 min of calcination in air at 350 °C, 400 °C and 450 °C. Then, all the films were hydrazine treated for 10 h. The concentration profiles in Fig. 8(a) shows that the degradation of MB is highest for the film calcined at 350 °C, and decreases with increasing temperature. Fitting a first-order kinetic model to the concentration profiles (Supplementary Information Fig. S10 (a)) yields rate coefficients for films calcined at 350 °C, 400 °C and 450 °C of 0.12 h⁻¹, 0.102 h⁻¹ and 0.09 h⁻¹, respectively. The trend probably reflects a tradeoff between crystallization during calcination and nitrogen doping / reduction during hydrazine treatment. At 350 °C, the films are likely to be least crystalline, and therefore most easily doped and reduced by species derived by hydrazine decomposition. Although increasing the calcination temperature would be expected to enhance the activity of the titania itself due to crystallization, it reduces the ease with which hydrazine modification of the matrix occurs, and the photocatalytic activity under visible illumination is reduced.

The effect of calcination time of the titania films on the photocatalytic activities of the 10 h_Ti³⁺-N-TiO₂ films was also studied by methylene blue degradation under BLED illumination. Three titania films were prepared with calcination in air at 350 °C for 10 min, 60 min and 120 min, followed by 10 h of hydrazine treatment. The concentration profiles in Fig. 8(b) shows that the degradation of the MB in this series is fastest for the film calcined for 10 min, and decreases with longer calcination. Fitting a first-order kinetic model to the concentration profiles (Supplementary

Information Fig. S10(b)) yields rate coefficients for 10 min, 60 min and 120 min calcined films of 0.12 h^{-1} , 0.064 h^{-1} and 0.052 h^{-1} , respectively. Longer calcination than the baseline 10 min used to decompose the pore template would be expected to induce greater crystallization of the titania, along with the possibility of pore sintering. Both effects would reduce the effectiveness of matrix modification by hydrazine treatment. Thus, consistent with the hypothesis that the disordered nature of sol-gel titania aids in hydrazine-based doping, brief (10 min), low temperature ($350\text{ }^{\circ}\text{C}$) calcination is found to give the best photocatalytic activity for films with 10 h hydrazine treatment.

Further, methylene blue degradation was performed with titania films calcined at $350\text{ }^{\circ}\text{C}$ for 10 min to test their photocatalytic activity under UVLED illumination. The $10\text{ h_Ti}^{3+}\text{-N-TiO}_2$ films showed higher photoactivity compared to the undoped TiO_2 film under both UVLED and BLED illumination as shown in Fig. 8(c). The sample and wavelength are indicated in the legend as (hydrazine treatment time)_(LED type), for example 10h_BLED indicating 10 h hydrazine treatment and BLED illumination. Fitting the concentration profiles (Supplementary Information Fig. S10(c)) gives rate constants for 0 h_BLED, 10 h_BLED, 0 h_UVLED and 10 h_UVLED films of 0.042 h^{-1} , 0.12 h^{-1} , 0.231 h^{-1} , and 0.243 h^{-1} , respectively. The photoactivities of both undoped and doped films under UVLED illumination are much higher than under BLED illumination. In addition, the hydrazine treated titania films showed a higher degradation rate than undoped titania films illumination at both wavelengths. According to previous studies, nitrogen doping does not improve photocatalytic activity under UV light irradiation, and may actually deteriorate UV photoactivity [31, 57, 59]. The reason that UV photoactivity is not lost in the $\text{Ti}^{3+}\text{-N-TiO}_2$ films here is due to efficient reduction and nitrogen doping of the titania matrix of the amorphous sol-gel TiO_2 . Efficient doping combined with advantageous mesoporous TiO_2 structure seems to enable efficient charge separation and transport.

Fig. 8. Concentration profiles during methylene blue degradation with 10 h_ Ti^{3+} -N-TiO₂ films showing (a) effect of calcination temperature of titania films, (b) effect of calcination time of titania films and (c) effect of light sources (BLED and UVLED).

To alleviate concerns over visible enhancement arising from sensitization by MB and to show the versatility of the doped films, photoelectrochemical (PEC) activity measurements were conducted in a three-electrode system to evaluate the water oxidation performance of the doped films as a photoanode. The current-time curves for the undoped TiO₂ and Ti^{3+} -N-TiO₂ films are presented in Fig. 9(a). The inset in Fig. 9(a) presents the enlarged region from 400 to 1800 s of the current-time plot. The initial currents for the doped films are significantly higher than the undoped TiO₂ film. The current increases with increasing hydrazine treatment period. However, the current decreases with time for all of the doped films. Ti^{3+} may be oxidized during the current-time experiment resulting in decreasing current.

For comparison of the photoelectrochemical performance of the doped films, the photocurrent was separated from the total current. The current vs. time data for all dark periods was fit with a single fourth order polynomial (Supplementary Information Fig. S11) and this function subtracted from the total current to give the photocurrent. Supplementary Information Fig. S12 shows the photocurrent as a function of time for the undoped and Ti^{3+} -N-TiO₂ films. It is clear that the photocurrent of the Ti^{3+} -N-TiO₂ films is higher than undoped TiO₂ films. The specific photocurrent was calculated from the photocurrent density divided by the mass per area (2.29×10^{-5} g/cm² calculated using 80 nm film thickness, and pore diameter and wall thickness from the SEM imaging). The specific photocurrent of undoped TiO₂ and Ti^{3+} -N-TiO₂ films at 600 s (the start of the second illuminated period) are plotted as a function of hydrazine treatment time in Fig. 9(b). The 10 h_ Ti^{3+} -N-TiO₂ films showed the maximum photocurrent which is about 4 times as high

as for undoped TiO_2 films. The photocurrent for the film after 20 hours of hydrazine treatment is lower than for the film treated for 10 hours. This is consistent with the maximum in photocatalytic activity for MB degradation at 10 hours of hydrazine treatment and can be explained by the mesostructure deterioration for more than 10 hours of hydrazine treatment as shown in Fig. 7. The enhancement in water oxidation of this study surpasses the results reported in previous studies. For instance, Xu et al. prepared hydrazine treated titania nanotubes and found $2\times$ enhancement in photoelectrochemical performance compared to undoped titania nanotubes in water oxidation under a halogen lamp [5]. Mao et al. also showed less than $2\times$ photocurrent enhancement in water oxidation under a solar simulator for hydrazine TiO_2 nanotubes compared to undoped TiO_2 nanotubes [1]. The greater enhancement found here may be a result of the ease with which the initially amorphous sol-gel titania film is doped by N_2H_4 treatment. The absolute current density of our titania film is relatively small compared to the current density of some other titania materials reported in literature [60]. This is because the films have low thickness (80 nm) and the BLED source has low energy density. It is difficult to make absolute comparison of the photocurrents obtained from photoelectrochemical water oxidation across different measurement systems in the literature because of differences in several factors including light source, wavelength and intensity; catalyst amount; addition of various reagents (e. g. hole scavengers); addition of co-catalysts (e.g. metal nanoparticles); electrolyte pH; and applied potential. The specific photocurrent per gram of our doped mesoporous titania was estimated to be on the scale of mA, which is quite significant considering the low intensity of the BLED source. The absolute photocurrent of our mesoporous titania thin films can be further improved by preparing thicker films using a layer-by-layer deposition technique to be reported in a future contribution.

Fig. 9. (a) Current density as a function of time for the water oxidation reaction with TiO_2 and $\text{Ti}^{3+}\text{-N-TiO}_2$ films (The inset is an expansion of the region from 400 to 1800 s) and (b) Photocurrent per mass of undoped TiO_2 and $\text{Ti}^{3+}\text{-N-TiO}_2$ films at 600 s as a function of hydrazine treatment time.

The electronic properties of the films and the film /electrolyte interface were investigated by electrochemical impedance spectroscopy (EIS) for undoped TiO_2 and $\text{Ti}^{3+}\text{-N-TiO}_2$ films. Mott-Schottky plots were prepared using data from the EIS measurement as shown in Fig. 10(a). The positive slope of the Mott-Schottky plot indicates that (as expected) TiO_2 is an n-type semiconductor [1, 61]. The flat band potential (E_{fb}) was estimated by extrapolating the linear

portion of the Mott-Schottky plot to the horizontal axis as shown in Supplementary Information Fig. S13. Fig. 10(b) shows that E_{fb} of Ti^{3+} -N-TiO₂ films decreases monotonically as a function of hydrazine treatment duration. E_{fb} represents the edge of the conduction band of TiO₂ since it is an n-type semiconductor, [62-66] so Fig. 10(b) suggests that a new energy band for the Ti^{3+} state might be formed just below the conduction band of TiO₂ due to the reduction by hydrazine. The Ti^{3+} state formation increases with the increasing hydrazine treatment time resulting in decreasing E_{fb} . This EIS measurement is consistent with the photocatalytic and photoelectrochemical results in that the photoactivity increases as E_{fb} of TiO₂ decreases due to hydrazine treatment. The downward shift of the edge of the conduction band is also in agreement with the band gap reduction of the Ti^{3+} -N-TiO₂ films estimated from optical measurement. It has suggested that nitrogen doping reduces E_{fb} [63, 64, 67], but Spadavecchia et al. demonstrated both experimentally and theoretically that nitrogen doping alone does not change E_{fb} [62]. Therefore, the observed change in E_{fb} is most likely caused by reduction due to the use of hydrazine as a source of nitrogen doping.

In an n-type semiconductor (TiO₂), electrons are the majority charge carriers. The charge carrier density (N_D) can be calculated from the slope of the linear portion of a Mott-Schottky plot using Equation 1 (the Mott-Schottky equation):

$$\frac{1}{C^2} = \left(\frac{2}{q\epsilon\epsilon_0 N_D} \right) \left(E - E_{fb} - \frac{\kappa T}{q} \right) \quad (1)$$

where C is the areal capacitance of the space charge layer, q the elementary charge (1.6×10^{-19} C), ϵ_0 the vacuum permittivity (8.85×10^{-14} Fcm⁻¹), ϵ the dielectric constant of the studied semiconductor, E_{fb} the flat band potential, E the applied external bias, κ Boltzmann's constant, and T the absolute temperature.

The dielectric constant is assumed to be 41 for TiO₂ [63]. The calculated value of N_D in the undoped mesoporous TiO₂ film is 9×10^{19} cm⁻³. Treatment with N₂H₄ caused a decrease in N_D for

5 and 10 hours of treatment (Fig. 10(c)), but N_D increased to $9.62 \times 10^{19} \text{ cm}^{-3}$ in the film treated for 20 hours. Since N_2H_4 is both a strong reducing agent and a nitrogen source, treatment introduces both Ti^{3+} electron donors (tending to increase N_D) [1] and nitrogen atom electron acceptors (tending to decrease N_D) [62, 67]. The balance of the two determined the net change in N_D , and excessive nitrogen doping has been suggested to convert Ti^{3+} to Ti^{4+} species [62]. Fig. 10(c) shows that introduction of acceptors dominates the properties of the 5 h Ti^{3+} -N- TiO_2 and 10 h Ti^{3+} -N- TiO_2 films resulting in lower N_D compared to undoped TiO_2 film. On the other hand, the increase in N_D in the 20 h Ti^{3+} -N- TiO_2 film suggests that prolonged treatment with hydrazine results in a net introduction of more Ti^{3+} compared to nitrogen. Hanzu et al. reported a reduction in N_D from $6.7 \times 10^{20} \text{ cm}^{-3}$ in undoped TiO_2 nanotubes to $3.9 \times 10^{20} \text{ cm}^{-3}$ upon nitrogen doping [62]. Mao et al. reported that N_D increased from $6.9 \times 10^{18} \text{ cm}^{-3}$ in titania nanowires to $8.54 \times 10^{19} \text{ cm}^{-3}$ after 24 hours of N_2H_4 treatment [1]. The results found here are consistent with these two observations if we conclude that nitrogen introduction dominates N_D at short times and titanium reduction takes over the electronic properties of the films at long treatment times.

Fig. 10. (a) Mott-Schottky plots for undoped TiO_2 and $\text{Ti}^{3+}\text{-N-TiO}_2$ films, and (b) flat band potential and (c) charge carrier density of the films as a function of hydrazine treatment time.

4. Conclusions

Titanium (Ti^{3+}) and nitrogen co-doped cubic ordered mesoporous TiO_2 thin films were prepared by hydrazine treatment and tested for photocatalysis under visible light illumination. The cubic ordered mesoporous TiO_2 thin films were prepared by a surfactant templated sol-gel method followed by hydrazine treatment in a closed vessel to allow long-term exposure to hydrazine from the vapor phase. Both interstitial and substitutional nitrogen were found inside of the doped films whereas no nitrogen was found in the undoped TiO_2 film. XPS and optical characterization suggest that the band gap of TiO_2 films was reduced from 3.5 eV (in undoped TiO_2 films due to their amorphous / nanocrystalline structure) down to a minimum of 3.3 eV after the hydrazine treatment. While this band gap reduction does not bring the primary absorption into the visible wavelength range, enhanced visible light absorption was found in an absorbance tail that extended well into the visible wavelength range, most likely due to the formation of localized absorbers that may function as catalytic sites at the surface of the mesoporous titania.

Photocatalytic degradation tests with methylene blue (MB) demonstrated a significant enhancement in photocatalytic activity of the Ti^{3+} -N- TiO_2 films over undoped TiO_2 films under visible-light illumination. A 455 nm LED was used as a representative visible light source for the experiment because this wavelength is not absorbed by MB. The Ti^{3+} -N- TiO_2 film prepared by 10 hours of hydrazine treatment showed the optimal photocatalytic performance, with the determined rate coefficient of 0.12 h^{-1} , roughly 3 times greater than that of undoped TiO_2 films. Based on the film thickness, structure and illuminated area, this corresponds to a rate coefficient of $\sim 85 \text{ min}^{-1}/(\text{g catalyst})$. To confirm that the high level of photocatalytic enhancement observed here can be attributed to the use of disordered sol-gel TiO_2 , the effects of increasing calcination temperature and time were observed. Both were found to decrease photocatalytic activity, showing

that 350 °C and 10 min are the optimum calcination conditions for introducing visible-light photocatalytic activity by hydrazine treatment in these films. The enhancement in photoactivity of the film was confirmed by measuring photoelectrochemical (PEC) water oxidation. The Ti^{3+} -N- TiO_2 films prepared with 10 hours of hydrazine treatment also showed optimal performance in the PEC experiments, roughly four times the photocurrent of undoped TiO_2 films. This study thus demonstrates the effectiveness of hydrazine treatment as a source of Ti^{3+} and N dopant for mesoporous TiO_2 thin films prepared by surfactant templating. Treatment with hydrazine leads to improved photocatalytic and photoelectrochemical performance, but is balanced by gradual coarsening of the titania mesostructure due to exposure to hydrazine and water vapor during treatment.

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†Electronic Supplementary Information (ESI) available: Schematic of photocatalysis experiment, LED spectrum, STEM image, HRTEM image, SAED pattern, Tauc plots, XPS Ti 2p depth profile spectra, methylene blue adsorption kinetics results, first-order kinetics fitting, SEM images,

modeling of dark current, model equations for dark current, photocurrent-time curves, and Mott-Schottky plots.

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